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(54) Detergent composition containing low level of substituted polyamines.

(57) Detergent compositions containing low levels of substituted polyamines are disclosed. The polyamines are substituted by one long chain alkyl or alkenyl group and by at least two alkylene oxide radicals attached to different nitrogens. Preferred compositions produce a laundry liquor pH in the range from 8.5-12.0; and frequently contain water-soluble or water-insoluble detergent builders.

These compositions exhibit a broad range of textile treatment benefits particularly enhanced soil release and cleaning properties.

DETERGENT COMPOSITION CONTAINING LOW LEVEL OF SUBSTITUTED POLYAMINES

Technical Field

This invention relates to detergent compositions containing low levels of polyamines which are substituted by one long chain alkyl or alkenyl group and by at least two alkylene oxide, especially ethylene oxide, groups attached to different nitrogen atoms. These compositions, upon use in an alkaline laundry liquor, provide remarkable textile treatment benefits inclusive of soil release and cleaning properties.

There is a standing desire to improve textile cleaning and confer further textile benefits through either the laundry treatment or via the subsequent use, vs. the laundry treatment of an additive e.g. during the rinse.

U.S. Patent 3,985,923, Basadur, issued October 12, 1976, relates to the application of renewable soil release finish during the rinsing step from a dilute aqueous acidic solution. The release agent is a copolymer based on a dibasic carboxylic acid and a glycolic compound.

U.S. Patent 3,962,152, Nicol, Hays, issued June 8, 1976 pertains to the laundry treatment deposition of renewable soil release finish to synthetic fabrics treated therewith. The soil release finish consists of ethylene terephthalate and polyethylene oxide terephthalate.

The performance benefits derived from the utilization of the like additives are premised on the deposition of a

releasable coating onto the fiber from the laundry/rinsing step. The coating will be rinsed off during the next laundry cycle, inclusive of the total soil accumulated thereon, to thus provide a "non-alterated" degree of cleaning.

The use of substituted polyamines in detergent technology is also known. German patent application DOS 21 57 785 relates to the washing and softening of textiles with the aid of detergent composition containing anionic tensides and an alkoxylated N-monosubstituted alkane diamine softener which is frequently used in a level from 2-10%.

German Patent Applications : DOS 25 20 267, DOS 27 00 641 and DOS 27 03 020 all disclose mixtures of epoxylated mono- or polyamine, possibly alkoxylated, alkanes. These substances can serve as detergent corrosion inhibitors and cold-water detergents and are frequently used in additive levels up to 10%. German Patent Application DOS 22 26 871 discloses conventional detergent compositions containing a N-alkyl-polyhydroxyalkylamine greying-inhibitor which is usually obtained by reacting a N-alkyl-alkylendiamine with an aldose under reducing conditions followed by ethoxylation of the reaction product.

The utilization of substituted, possibly alkoxylated, polyamines as rinse softener is known from German Patent Applications: DOS 25 39 310 and DOS 26 31 114.

Belgian Patent 773.260 discloses a process for the combined washing and softening of textiles with the aid of detergent mixtures containing anionic surface-active agents, and N-alkylpropane-1,3-diamines. The detergent utilization of diamines is also known from a series of other references as e.g. represented by: U.S. Patent 3.494.870, Kersnar et al., issued February 10, 1970; French Patent 1.581.392; and German Patent Applications DOS 21 37 290; DOS 27 08 516; DOS 21 18 511; DOS 20 48 330; DOS 19 29 040; DOS 19 22 046. The state of the art as e.g. represented by the cited references is mostly suggestive of through-the-wash softening and other incidental textile benefits which are different

from the technology of this invention.

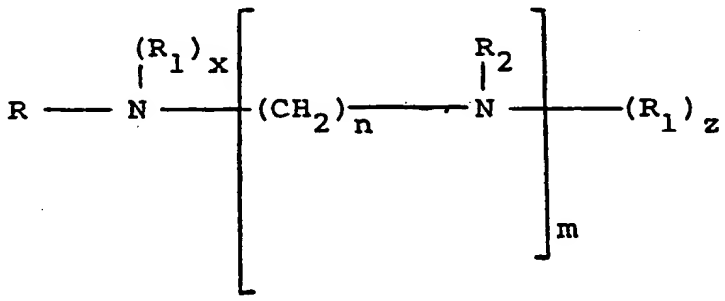
It is an object of the present invention to provide detergent compositions containing a surface-active agent and low levels of substituted polyamines; these compositions are capable of providing a broad range of textile treatment benefits, particularly enhanced soil release and cleaning properties.

SUMMARY OF THE INVENTION

The present invention comprises detergent compositions having enhanced soil release and cleaning properties containing

(a) from about 2% to about 60% by weight of a surface-active agent selected from the group consisting of anionic, nonionic, zwitterionic, and ampholytic detergents and mixtures thereof; and

(b) from 0.1% to 1.2% by weight of a polyamine having the formula:



wherein R is an alkyl or alkenylgroup having 10 to 22 carbon atoms, the R_1's, which are identical or different, are ethylene oxide or propylene oxide, R_2 is hydrogen, C_{1-4} alkyl or $(R_1)y$, where x, y, and z are numbers such that the sum (x+y+z) is in the range from 2 to about 25, is a number from 1 to about 6 and m is a number from 1 to about 9,

whereby a 1% aqueous solution of the composition has an alkaline pH (20°C).

In a preferred embodiment, the compositions herein are granular compositions having an alkaline pH in the range from about 8.5-11 (1% solution, 20°C). Such preferred granular

compositions frequently contain a peroxybleach agent. In another preferred embodiment the granular compositions herein are built detergent compositions wherein the builder system is comprised of a water-insoluble aluminosilicate, if desired, in combination with a water-soluble detergent co-builder.

DETAILED DESCRIPTION OF THE INVENTION

The detergent compositions of the present invention are defined in three essential parameters:

(a) a surface-active agent;

(b) a polyamine; and

(c) have an alkaline pH in 1% aqueous solution at 20°C.

Optional ingredients can be added to provide various performance and aesthetic benefits. The granular detergent executions of this invention frequently comprise a peroxybleach ingredient in the usual levels, i.e., in the range from about 3% to about 50% by weight, and a builder or co-builder system as defined in more detail hereinafter.

Unless indicated to the contrary, the "percent" indications hereinafter stand for "percent by weight".

The detergent compositions in accordance with this invention can be in any conventional state inclusive of liquid pasty and solid executions. Preferred are granular executions.

SURFACE-ACTIVE AGENT

The detergent compositions herein comprise, as a first essential component, a surface-active agent selected from the group consisting of anionic, nonionic, zwitterionic and ampholytic detergents and mixtures thereof.

The surface-active agents normally represent from 2% to 60% of the detergent composition

The preferred granular peroxybleach-containing built detergents herein usually contain from about 2% to about 25%, preferably from about 5% to about 20% of organic surface-active agents. Liquid executions of this invention frequently contain surface-active agents in a level

from about 10% to about 50%, preferably from 15% to 40%.

Suitable organic surface-active agents herein can be represented by active ingredients which are known to meet the requirements for use in and/or have already been used in detergent compositions. Exemplifying species for use herein can be selected from the group of anionic, nonionic, ampholytic, zwitterionic, surfactants and mixtures thereof.

Examples of suitable nonionic surfactants include:

(1) The polyethylene oxide condensates of alkyl phenols. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbons atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol.

(2) The condensation products of aliphatic alcohols with ethylene oxide. The alkyl chain of the aliphatic alcohol may either be straight or branched and generally contains from about 8 to about 22 carbon atoms. Examples of such ethoxylated alcohols include the condensation product of about 6 moles of ethylene oxide with 1 mole of tridecanol, myristyl alcohol condensed with about 10 moles of ethylene oxide per mole of myristyl alcohol, the condensation product of ethylene oxide with coconut fatty alcohol wherein the coconut alcohol is a mixture of fatty alcohols with alkyl chains varying from 10 to 14 carbon atoms and wherein the condensate contains about 6 moles of ethylene oxide per mole of alcohol, and the condensation product of about 9 moles of ethylene oxide with the above-described coconut alcohol.

(3) The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. The condensation product frequently contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000.

Examples of suitable ampholytic synthetic detergents are sodium 3-(dodecyl-amino)-propionate, and sodium 3-(dodecyl-

amino)propane-1-sulfonate.

Zwitterionic surfactants for use herein include 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate, 3-(N,N-dimethyl-N-alkylammonio)-2-hydroxypropane-1-sulfonate, the alkyl group being derived from tallow fatty alcohol; 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate; 3-(N,N-dimethyl-N-tetradecylammonio)propane-1-sulfonate; and 3-(N-N-dimethyldodecylammonio)-2-hydroxypropane-1-sulfonate.

Suitable anionic detergents include ordinary alkali metal soaps of higher fatty acids containing from about eight to about 24 carbon atoms and preferably from about 10 to about 20 carbon atoms.

Alkyl sulfonated or sulfated surfactants inclusive of alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 20 carbon atoms in straightchain or branched-chain configuration, e.g., those of the type described in U.S. Patent No. 2,220,099 and 2,477,383 (especially valuable are linear straight chain alkyl benzene sulfonates in which the average of the alkyl groups is about 11.8 carbon atoms and commonly abbreviated as $C_{11.8}$ LAS); sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates also represent a class of very useful anionic surface-active agents.

Useful in this invention are also salts of 2-acyloxy-alkane-1-sulfonic acids.

Typical examples of the 2-acyloxy-alkanesulfonates are described in Belgium Patent No. 650,323 issued July 9, 1963, U.S. Patent Nos. 2.094.451 issued September 28, 1937 to Guenther et al., and 2.086.215 issued July 6, 1937 to DeGroote; these references are hereby incorporated by reference.

β-alkoxy alkane sulfonates can also be used. Specific examples of β-alkyloxy alkane sulfonates having low hardness (calcium ion) sensivity useful herein to provide superior cleaning levels under household washing conditions include: potassium-β-methoxydecanesulfonate, sodium 2-methoxytridecane-

sulfonate, potassium 2-ethoxytetradecylsulfonate, and sodium 2-isopropoxyhexadecylsulfonate.

Paraffin sulfonates containing a straight or branched chain, saturated aliphatic hydrocarbon radical having form 8 to 24, preferably 12 to 18, carbon atoms can also be used.

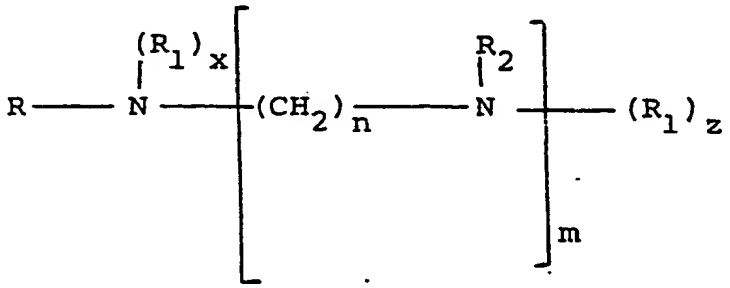
Other synthetic anionic detergents useful herein are alkyl ether sulfates. These materials have the formula $RO(C_2H_4O)_xSO_3M$ wherein R is alkyl or alkenyl of about 10 to about 20 carbon atoms, x is 1 to 30, and M is a water-soluble cation.

Suitable examples of alkyl ether sulfates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from about 12 to about 16 carbon atoms and an average degree of ethoxylation of from about 1 to 4 moles of ethylene oxide. Such a mixture also comprises from about 0 to 20% by weight C_{12-13} compounds; from 60 to 100% by weight of $C_{14-15-16}$ compounds; from 0 to 20% by weight of $C_{17-18-19}$ compounds; from about 3 to 30% by weight of compounds having a degree of ethoxylation of 0; from about 45 to 90% by weight of compounds having a degree of ethoxylation of from 1 to 4; from about 10 to 25% by weight of compounds having a degree of ethoxylation of from 4 to 8; and from about 0.1 to 15% by weight of compounds having a degree of ethoxylation greater than 8.

α-Olefin sulfonate mixtures as described in U.S. Patent No. 3.332.880, issued July 25, 1967, incorporated herein by reference, can also be used.

THE POLYAMINE

A second essential component in the compositions herein is represented by a polyamine having the formula



wherein R is an alkyl or alkenylgroup having 10 to 22 carbon atoms, the R_1's, which are identical or differe are ethylene oxide or propylene oxide, R_2 is hydrogen, C_{1-4} alkyl or $(R_1)y$, where x, y, and z are numbers suc that the sum (x+y+z) is in the range from 2 to about 2 is a number from 1 to about 6, preferably from 2 to 4, and m is a number from 1 to about 9, preferably 1 or 2. This polyamine component is used in a level from 0.1% to 1. preferably from 0.25% to 0.75%. Utilizing less than the minimum levels will not provide anymore the inventive benef whereas levels above the specified definition will not yiel anymore performance advantages but rather unexpectedly caus noticeable cleaning performance negatives, particularly whiteness deficiencies.

Suitable species of the polyamine component for use he correspond to the general formula above wherein the individ substituents can be varied as follow:

R : tallow C_{16-18} alkyl; coconut C_{12-14} alkyl; lauryl; palmityl; stearyl; oleyl.

R_1: ethylene oxide

R_2: C_{1-4} alkyl (especially : CH_3-, C_2H_5-); ethylene oxide.

n is equal to 2 or 3;

m is equal to 1, 2 or 3;

x,y,z are each 1, 2, 3 or 4 and their sum is from 3 to 18.

Where m=1, R_2 is desirably a C_{1-4} alkyl or ethylene oxide group.

Preferred polyamines for use herein are defined by the following substituents:

R: hydrogenated tallow C_{16-18} alkyl;

R_1: ethylene oxide;

R_2: ethylene oxide;

n : 3;

m : 1 or 2;

x, y, z are each at least 1 and their sum is in the range fr 3 to 12, for example 3,7 and 12.

A preferred polyamine for use in built peroxybleach containing detergents is N-hydrogenated tallow C_{16-18}-N,N',N

tri-(2-hydroxyethyl)-propylene-1,3-diamine.

ALKALINE SOLUTION

The compositions herein shall yield upon dissolution in water an alkaline laundry liquor. Preferably, a 1% aqueous solution shall have an alkaline, preferably in the range from about 8.5 to about 12, pH measured at 20°C. The pH can be adjusted by known means inclusive of alkaline buffer substances such as alkali hydroxides, ammonium hydroxide, amine and substituted amines, such as mono-, di- and triethanolamines; alkaline builder substances such as alkalimetal carbonates, alkalimetal phosphates and polyphosphates and alkalimetal silicates. The proper choice of suitable pH adjusting agents shall of course take into account the physical state --liquid, pasty, solid-- of the composition and the relative compatibility of the additional ingredients of a particular composition. Such ingredient optimization and selection are well-known routine measures, however.

OPTIONAL INGREDIENTS

As noted earlier, solid compositions, particularly those containing a bleaching system are especially preferred in the context of this invention. The peroxybleach component in these preferred compositions is frequently used in an amount from about 3% to about 50%, preferably from about 8% to about 35%. Suitable peroxybleach compounds are all those which are known to be adapted for use in or have already been used in detergent technology. Examples of such peroxybleaches include the water-soluble alkali salts of perborate mono-hydrate, perborate tetrahydrate, persulfates, persilicates, perphosphates, and percarbonates. Organic oxygen-bleach activators can also advantageously be used in the oxygen-bleach containing detergent executions of this invention. Examples of such activators include phthalic anhydride, tetra-acetyl ethylene diamine, tetra-acetyl methylene diamine and tetra-acetyl glycouril. Such activators are frequently used in levels from about 0.2% to 15%, preferably from 1% to 4%.

The detergent compositions of this invention further frequently contain as optional ingredient, a detergent builder in a level from about 1% to about 50%. The non-solid detergent embodiments frequently contain builder ingredients in levels from e.g. 2% to 8%. The peroxybleach containing solid detergents contain detergent builders or a detergent builder system in a level which is frequently in the range from about 10% to about 45%. The builder component can be represented by all known water-soluble and water-insoluble detergent builder ingredients.

Non-limiting examples of suitable water-soluble, inorganic alkaline detergency builder salts include the alkali metal carbonates, borates, phosphates, polyphosphates, tripolyphosphates, bicarbonates, silicates, and sulfates. Specific examples of such salts include the sodium and potassium tetraborates, bicarbonates, carbonates, tripolyphosphates, pyrophosphates, and hexametaphosphates.

Examples of suitable organic alkaline detergency builder salts are : (1) water-soluble amino polyacetates, e.g. sodium and potassium ethylene diamine tetra-acetates, nitrilotriacetates, and N-(2-hydroxyethyl)nitrilodiacetates; (2) water-soluble salts of phytic acid, e.g. sodium and potassium phytates; (3) water-soluble polyphosphonates, including sodium, potassium and lithium salts of ethane-1-hydroxy-1,1-diphosphonic acid; sodium, potassium, and lithium salts of methylene-diphosphonic acid and the like. Additional organic builder salts useful herein include the polycarboxylate materials described in U.S. Patent No. 2.264.103, including the water-soluble alkali metal salts of mellitic acid. The water-soluble salts of polycarboxylate polymers and copolymers such as are described in U.S. Patent No. 3.308.067, incorporated herein by reference, are also suitable herein.

It is to be understood that while the alkali metal salts of the foregoing inorganic and organic polyvalent anionic builder salts are preferred for use herein from an economic standpoint, the ammonium, alkanolammonium (e.g. triethanol-

ammonium, diethanolammonium and monoethanolammonium) and other water-soluble salts of any of the foregoing builder anions can be used.

Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is disclosed in Canadian Patent No. 755,038, e.g., a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate, and trisodium ethane-1-hydroxy-1,1-diphosphonate.

Another type of detergency builder material useful in the present invention comprises a water-soluble material capable of forming a water-insoluble reaction product with water hardness cations, preferably in combination with a crystallization seed which is capable of providing growth sites for said reaction product. Specific examples of materials capable of forming the water-insoluble reaction product include the water-soluble salts of carbonates, bicarbonates, sesquicarbonates, silicates, aluminates and oxalates. The alkali metal, especially sodium, salts of the foregoing materials are preferred for convenience and economy. Preferred crystallization seed materials are calcium carbonate, calcium oxide and calcium hydroxide. Such "seeded builder" compositions are fully disclosed in British Patent Specification No. 1.424.406, incorporated herein by reference.

Non-seeded precipitating builder systems employing pyrophosphates or mixtures thereof with orthophosphates are also useful herein. Precipitating pyrophosphate and ortho-pyrophosphate builder systems are disclosed in German Patent Applications OLS No. 25 42 704 and 26 05 052 published April 15 and August 16, 1976, respectively, which are specifically incorporated herein by reference.

Suitable examples water-insoluble detergent builders are selected from the group consisting of zeolites A, X, or P(B). or mixtures thereof, having a particle size diameter of from about 0.01 micron to about 25 microns and containing at least 10% water of hydration, and amorphous hydrate aluminosilicate material of the empirical formula: $M_z(zAlO_2 \cdot ySiO_2)$ wherein M

is sodium, potassium ammonium, z is from about 0.5 to about 2, y is 1, said material having a particle size diameter of less than about 100 microns, a magnesium ion exchange capacity of at least about 50 milligrams equivalents of $CaCO_3$ hardness per gram of anhydrous aluminosilicate, and a Mg^{++} exchange rate of at least about 1 grain/gallon/minute/ gram/gallon, and mixtures thereof.

The preferred synthetic crystalline aluminosilicate materials for use herein commonly known as Zeolites A, X, and P(B) should contain at least 10% water of hydration and should have a particle size diameter of from about 0.5 micron to about 10 microns, more preferably from about 0.5 micron to about 2 microns. Aluminosilicate materials are more fully described in U.S. Patent 4,096,081, Phenicie et al., issued June 20, 1978, and German Patent No. 27 04 003, Ohren, published on August 18, 1977, the disclosures of which are incoporated herein by reference. The amorphous aluminosilicate materials suitable for use herein are fully described in U.S.Patent No. 4.180.485, Llenado, published December 25, 1979, incorporated herein by reference.

The water-insoluble detergent builders are frequently and preferably utilized in the granular compositions herein in conjunction with a water-soluble detergent cobuilder ingredient in a weight ratio of aluminosilicate:water-soluble detergent cobuilder of from 4:1 to 1:4. Suitable examples of preferred water-soluble cobuilder ingredients are represented by the water-soluble salts of nitrilotriacetic acid, polyphosphates e.g. tripolyphosphates, and citrates. The cations of these cobuilders can e.g. be represented by alkalimetal ions, sodium, potassium, lithium, and by organic ions such as amines, substituted amines (alkanolamines) and ammonium ions.

In addition to the components described hereinbefore, the compositions of this invention can comprise a series of supplementary components to perfect and complement the benefits derived from the compositions herein. These additional components include brighteners, dyes, perfumes, bactericides,

processing aids, anti-oxidants, corrosion inhibitors, enzymes suds regulants and so on.

It may be desirable to add a copolymer of a (1) vinyl compound having the general formula RCH = CHR wherein one R represents a hydrogen atom and the other R represents an alkyl radical containing from one to about 4 carbon atoms; and (2) maleic anhydride. The copolymeric vinyl ingredient is normally used in an amount from about 0.1% to about 6%, preferably from 0.25% to 4%. Specific examples of these copolymeric ingredients include a water-soluble acid, an alkali-metal salt of that acid, an ester, or a C_{1-2}alkyl- or alkylolamide of a maleic anhydride-vinyl C_{1-4} alkyl ether copolymer. The specific viscosity of, for example, the maleic anhydride-vinyl C_{1-4} alkyl ether, preferably methylether, copolymer for use herein normally varies between 0.1 and 6, most preferably between 0.2 and 5.0. The (molecular) monomer ratio (maleic: vinylalkylether) is preferably in the range from 2:1 to 1:2. The specific viscosity is defined by measuring the viscosity of the solution of 1 g of the anhydride copolymer in 100 ml methylethylketone at 25°C in a series.100 CANNON-FENSKE viscosity meter. The copolymeric component can serve as slurry processing aid to thus provide a detergent product having improved physical properties including flowability.

Another optional ingredient is a mixture of alkoxylated mono-and diesters of phosphoric acid. This mixture which is normally used in an amount from 0.5% to 20% by reference to the sum of the surface-active agents, is particularly useful in detergent compositions containing, in part or solely, nonionic surface-active agents. These phosphoric esters are preferably represented by alkoxylated fatty alcohols having from 10 to 22 carbon atoms with 2 to 15 moles ethylene oxide or propylene oxide. The weight ratio of monophosphoric esters to diphosphoric esters is usually in the range from 6:1 to 3:1, preferably 4:1.

It may be desirable, especially if nonionic surfactants are incorporated by slurrying and subsequent spray-drying, to

add to the crutcher from 0.01% to 10%, expressed by reference to the nonionic surfactant of, an anti-oxidant. Suitable examples of anti-oxidant materials are disclosed in German Patent Application DAS 16 17 209. A preferred anti-oxidant material is 4,4'-thiobis(6-tert-butyl-m-cresol).

The detergent compositions can additionally contain an enzymatic ingredient. Proteases, amylases and lipases can be added in an amount from 0.001% to about 5% to augment and aid in the cleaning activity of the detergent compositions herein. Preferred proteolytic enzymes are disclosed in Belgian Patent 775.854, to EYMERY et al., granted May 26, 1972.

The detergent compositions of this invention frequently comprise a suds regulant in a level of 0.01%-10%.

Suitable suds regulants are well-known in detergent technology and most of these can easily be used in combination with the claimed technology.

Conventional detergent suds regulants which can be used include saturated fatty acids especially those having 16 to 24 carbon atoms in the alkylchain, nonionic suds regulan and mixtures thereof. Another class of well-known suds regulants are silicones, preferably silanated silicones in admixture with microcrystalline waxes. Mixtures of low levels of silicones (0.01-0.2%) and/or fatty acids (0.2-2%) are known to be suitable for use in the liquid executions of this invention.

Preferred suds regulants containing a separately processed detergent additive on basis of a water-insoluble liquid hydrocarbon, an adjunct material preferable a solid hydrocarbon, and a hydrophobic silica are described in U.S. Patent 4,192,761, Peltre and Lafleur, issued March 11, 1980, incorporated herein by reference.

The following examples illustrate the invention and facilitate its understanding.

A granular detergent base-powder having the composition ed hereinafter was repared by conventional spray-drying of ...ry of the ind...dual ingredients, except the diamine and

sensitive ingredients as referred to hereinafter.

INGREDIENTS	Composition A	Example I
Linear dodecylbenzene-sulfonate sodium salt	5.6	5.6
Tallow alcohol sulfate sodium salt	2.4	2.4
Sodium tripolyphosphate	24.0	24.0
Sodium silicate solids (SiO_2:Na_2O=1.6)	6.0	6.0
Carboxymethylcellulose	1.0	1.0
Copolymer of maleic anhydride and methyl vinyl ether	1.0	1.0
Sodium sulfate	18.0	18.0
Moisture	7.0	7.0

A series of spray-drying sensitive ingredients were added to the above base-powder by dry-mixing, namely:

perborate tetrahydrate	32.0
enzyme	0.3
minors inclusive of perfume	2.2
suds regulant particles having the composition of example I of U.S. Patent 4.192.761	0.3

0.35% of N-hydrogenated tallow-N,N',N'-tri-(2-hydroxy-ethyl)-propylene-1,3-diamine was sprayed onto the mixture of the base-powder and the spray-drying sensitive ingredients.

These detergent compositions were then used for comparative laundry tests in a Miele W 421 washing machine.

Terry, undershirt and muslin cotton tracers were used to measure the comparative whiteness maintenance performance after 8 cumulative cycles.

Testing parameters were : 90°C heat-up cycle; pre-wash step and main-wash step using a product concentration of 0.9% in city water with an average water hardness of about 3 mmoles/l; ratio Ca/Mg = 5:1; laundering treatment in presence

of 3 kg soiled clothes.

After having been subjected to the above washing treatment (8 cumulative cycles) the dried whiteness maintenance tracers were visually graded by two expert judges thereby using a 0-4 scale whereby:

0 = see no difference between the swatches
1 = believe there is a difference between the swatches
2 = there is a difference between the swatches
3 = am sure there is a difference between the swatches
4 = very important difference between the swatches.

The whiteness maintenance readings were pooled and averaged on 4 replicates with the following results. The swatches treated with composition A were used for reference purposes:

Tracer	Example I
Terry	+ 1.5
Undershirt	+ 1.4
Muslin	+ 0.5

+ means that example I is preferred over composition A.

These testing results confirm the consistent superiority of example I in accordance with this invention versus prior art composition A.

Substantially identical results are obtained from the composition of example I wherein the tallow-diamine is substituted by a substantially comparable level of a polyamine selected from N-coconut-N,N',N'-tri-(2-hydroxyethyl)-propylene-1,3-diamine; N-palmityl-N,N',N'-hepta-(2-hydroxyethyl)-ethylene-1,2-diamine; N-lauryl-N'-methyl-N,N'-tri-(2-hydroxyethyl)-propylene-1,3-diamine.

Granular detergent compositions were prepared as described for example I (thereby using the same polyamine) in the following proportions:

INGREDIENTS	EXAMPLES II	III	IV	COMPOSITI B
Polyamine	0.25	0.5	0.75	2.0
Linear dodecylbenzene sulfonate sodium salt	5.6	5.6	5.6	5.6
Tallow alcohol sulfate sodium salt	2.4	2.4	2.4	2.4
Sodium tripolyphosphonate	24.0	24.0	24.0	24.0
Sodium silicate solids (SiO_2:Na_2O = 1.6)	6.0	6.0	6.0	6.0
Carboxymethylcellulose	1.0	1.0	1.0	1.0
Copolymer of maleic anhydride and methyl vinyl ether	1.0	1.0	1.0	1.0
Perborate tetrahydrate	32.0	32.0	32.0	32.0
Enzyme	0.3	0.3	0.3	0.3
Minors inclusive of perfume	2.5	2.5	2.5	2.5
Suds regulant of example I	0.3	0.3	0.3	0.3
Sodium sulfate, moisture	bal.	bal.	bal.	bal.

The testing conditions were identical to those describ in example I.

Whiteness maintenance readings were pooles and average 4 replicates with the following results. Swatches treated example II (in accordance with this invention) were used fo reference purposes.

TRACER	EXAMPLES II (Ref.)	III	IV	COMPO-SITION B
Terry	0	+1.0	+0.8	-1.1
Undershirt	0	+1.9	+1.2	-1.1
Muslin	0	+1.3	+1.1	-1.3

+ means the relevant example composition is preferred over example II.

These comparative results show the criticality of the claimed level limitations in reference to composition B containing 2% of the polyamine.

Granular detergent compositions containing a co-builder system were prepared comprising the following ingredients:

INGREDIENTS	COMPOSITION C	EXAMPLE V
Linear dedecylbenzene sulfonate sodium salt	5.6	5.6
Tallow alcohol sulfate sodium salt	2.4	2.4
Sodium tripolyphosphate	16.0	16.0
Sodium aluminosilicate (zeolite A)*	18.0	18.0
Sodium silicate solids (SiO_2:Na_2O= 1.6)	6.0	6.0
Carboxymethylcellulose	1.0	1.0
Perborate tetrahydrate	32.0	32.0
Enzyme	0.6	0.6
Minors inclusive of perfume	2.5	2.5
Polyamine (as defined in example I)	-	0.35
Sodium sulfate, moisture	bal.	

* fully hydrated, average particle diameter 2-8 microns.

The testing conditions were identical to those described in example I hereinbefore.

Whiteness maintenance readings after 4 cumulative cycles were pooled and averages on 4 replicates with the following results.

Swatches treated with prior art composition C were used for reference purposes:

TRACER	EXAMPLE V
Undershirt	+1.3
Muslin	+2.0

+ means that example V is preferred over composition C.

These results illustrate the performance benefits deliver d by this invention in an aluminosilicate cobuilt

detergent composition.

A series of additional compositions of this invention we prepared with the aid of the composition of example I, except for the variation in the degree of ethoxylation (x+y+z) of th polyamine.

	COMPOSITION D	EXAMPLES VI	VII
Degree of ethoxylation (x + y+ z)	0	7	12

Testing conditions were identical to those described in example I. Whiteness maintenance readings were pooled and averaged on 4 replicates with the following results. Swatche: treated with Composition D were used for reference purposes.

TRACER	COMPOSITION D	EXAMPLES VI	VII
Terry	0	+1.5	+2.1
Undershirt	0	+2.5	+2.4
Muslin	0	-	+2.1

+ means the relevant composition is preferred over composition D.

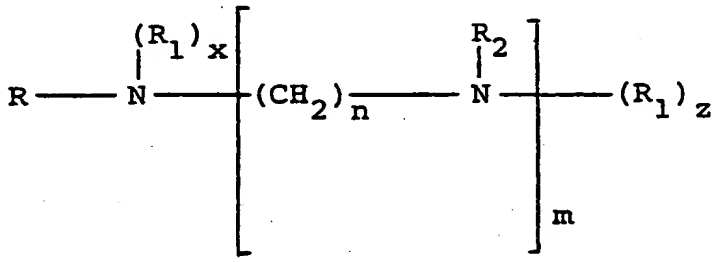
The above testing results show that the performance benefits can not be obtained from non (low) alkoxylated polyamines and also that the degree of ethoxylation can be varied without adversely affecting the performance benefits.

CLAIMS

1. A detergent composition having enhanced soil release and cleaning properties comprising:

(a) from about 2% to about 60% by weight of a surface-active agent selected from the group consisting of anionic, nonionic, zwitterionic, and ampholytic detergents and mixtures thereof; and

(b) from 0.1% to 1.2% by weight of a polyamine having the formula:



wherein R is an alkyl or alkenylgroup having 10 to 22 carbon atoms, the R_1's, which are identical or different, are ethylene oxide or propylene oxide, R_2 is hydrogen, C_1-C_4 alkyl or $(R_1)y$, where x, y, and z are numbers such that the sum (x+y+z) is in the range from 2 to about 25, n is a number from 1 to about 6 and m is a number from 1 to about 9,

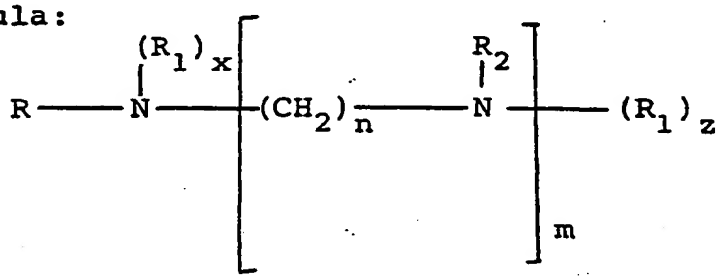
whereby a 1% aqueous solution of the composition has an alkaline pH (20°C).

2. The composition in accordance with Claim 1 wherein the polyamine is present in an amount from 0,25% to 0,75% by weight, said polyamine being defined by the following substituents: R_2 is $(R_1)_y$, the R_1's are ethylene oxide, x,y, and z are each at least 1 and their sum is in the range from 3 to 12, m is 1 or 2, n is 3 and R is an alkyl group having from about 12 to about 18 carbon atoms.

3. A particulate detergent composition having enhanced soil release and cleaning properties comprising:

(a) from about 2% to about 25% by weight of a surface-active agent selected from the group consisting of anionic, nonionic, zwitterionic, and ampholytic detergents and mixtures thereof; and

(b) from 0.1% to 1.2% by weight of a polyamine having th formula:



wherein R is an alkyl or alkenylgroup having 10 to 2 carbon atoms, the R_1's, which are identical or different, are ethylene oxide or propylene oxide, R_2 is hydrogen, C_{1-4} alkyl or $(R_1)y$, where x, y, and z are numbers such that the sum (x+y+z) is in the rang from 2 to about 25, n is a number from 1 to about 6 and m is a number from 1 to about 9;

(c) from about 3% to about 50% by weight of a peroxyblea compound; and

(d) from about 1% to about 50% by weight of a detergent builder;

whereby a 1% aqueous solution of the composition, measured at 20°C, has a pH in the range from about 8.5 to about 12.

4. The composition in accordance with Claim 3 wherein th polyamine is present in an amount from 0.25-0.75% by weight, said polyamine being defined by the following substituents: R_2 is $(R_1)_y$, the R_1's are ethylene oxide, x, y and z are each at least 1 and their sum is in the range from 3 to 12, m is 1 or 2, n is 3 and R is an alkyl group having from about 12 to abou 18 carbon atoms.

5. The composition in accordance with Claim 3 wherein t peroxybleach component is present in an amount from about 8% about 35% by weight and is selected from the group consisting of water-soluble salts of perborate monohydrate, perborate tetrahydrate, persulfates, persilicates, perphosphates and percarbonates, and mixtures thereof.

6. The composition in accordance with Claim 3 wherein t detergent builder is present in an amount from about 10% to about 45% by weight.

7. The detergent composition in accordance with Claim 3 which in addition contains from 0.01% to 10% of a detergent suds regulant.

8. The detergent composition in accordance with Claim 6 wherein the detergent builder is a mixture of

(i) a water-soluble detergent builder selected from the gro consisting of the water-soluble salts of nitrilotriaceti acid, polyphosphates and citrates; and

(ii) a synthetic crystalline water-insoluble aluminosilicate builder material selected from the group consisting of zeolite A, zeolite X and zeolite P(B), said aluminosili-cate material containing at least 10% by weight of the silicate of water of hydration and having a particle siz diameter in the range from 0.5 micron to 10 microns;

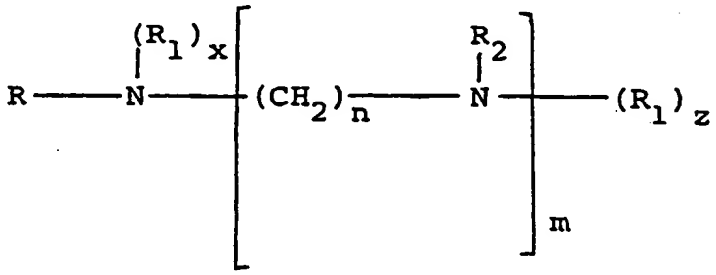
whereby the weight ratio of the water-soluble detergent builder: water-insoluble aluminosilicate builder is in the range from about 4:1 to about 1:4.

9. The composition in accordance with Claim 8 wherein tl polyamine is represented by N-hydrogenated tallow-N,N',N'-tri-(2-hydroxyethyl)-propylene-1,3-diamine.

10. A liquid de- rgent composition having enhanc d soil r-.-ea:e and clear-.-g properties ccmprising:

(a) from about 10% to about 50% by weight of a surface-acti agent selected from the group consisting of anionic, nonionic, zwitterionic, and ampholytic detergents and mixtures thereof; and

(b) from 0.1% to 1.2% by weight of a polyamine having the formula:



wherein R is an alkyl or alkenylgroup having 10 to 22 carbon atoms, the R_1's, which are identical or differen are ethylene oxide or propylene oxide, R_2 is hydrogen, C C_4 alkyl or $(R_1)y$, where x, y, and z are numbers such th the sum (x+y+z) is in the range from 2 to about 25, n is a number from 1 to about 6 and m is a number from 1 to about 9; and

(c) water,

whereby a 1% aqueous solution of the composition has an alkaline pH, measured at 20°C.

HE:rmr

European Patent Office

EUROPEAN SEARCH REPORT

0042187

Application number

EP 81 20 0600.5

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
P	EP - A1 - 0 023 367 (PROCTER & GAMBLE LTD.) * claims 4 to 6; page 23, examples 11 to 13; page 24, examples 14 to 17 --	5-8
D	US - A - 4 180 485 (PROCTER & GAMBLE CO.) * claims 1 and 4; column 4, lines 45 to 55; column 6, lines 26 to 32, column 11, lines 10 to 19 * --	5,8
D	DE - A - 2 118 511 (HENKEL & CIE.) --	
D	DE - A - 2 137 290 (HENKEL & CIE.) & GB - A - 1 356 827 --	
D	DE - A1 - 2 631 114 (PROCTER & GAMBLE CO.) & US - A - 4 126 562 --	
A	US - A - 3 959 378 (HENKEL & CIE.) --	
A	US - A - 4 080 162 (COLGATE-PALMOLIVE CO.) ----	

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

C 11 D 3/30
C 11 D 3/00
C 11 D 3/12

TECHNICAL FIELDS SEARCHED (Int. Cl.³)

C 11 D 3/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	23-07-1981	SCHULTZE